REACTIVE ETCHING AND OVERLAYER GROWTH WITH IONS AND MOLECULAR BEAMS

FINAL PROGRESS REPORT

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13. ABSTRACT (Maximum 200 words)

This program focused on issues related to material removal from a surface by either physical sputtering or chemical etching. Scanning tunneling microscopy was used to gain atomic-level insights into structural changes associated with surface modification. Studies that involved sputtering showed that novel surface morphologies could be produced and that enhanced epitaxial growth could be achieved on these modified surfaces. Studies that emphasized chemical etching showed that it was possible to tune the possible reaction pathways by varying the surface temperature and the concentration of the etchant. Studies of assisted-etching of GaAs demonstrated the effects of laser irradiation in both photochemical and photothermal processes. Finally, studies of electron irradiation showed surface damage by 2000 eV electrons related to vacancy creation. Results from these studies have direct relevance to technologies that depend on thin film formation (growth) and material removal (etching).

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List of manuscripts submitted or published:

1. X-S. Wang, R.J. Pechman, and J.H. Weaver, “Ion Sputtering of GaAs(110): From Individual Bombardment Events to Multilayer Removal,” J. Vac. Sci. Technol. B 13, 2031-2040 (1995).

2. X.-S. Wang, J. Brake, R.J. Pechman, and J.H. Weaver, “Effect of Ion Sputtering on Ge Epitaxy on GaAs(110),” Appl. Phys. Lett. 68, 1660-1662 (1996).

3. X.-S. Wang, R.J. Pechman, and J.H. Weaver, “Trends in Surface Roughening: STM Analyses of Ion-sputtered GaAs(110),” Surf. Sci. **364**, 511-518 (1996).

4. J. Brake, X.-S. Wang, R.J. Pechman, and J.H. Weaver, “Enhanced Epitaxial Growth on Substrates Modified by Ion Sputtering: Ge on GaAs(110),” Phys. Rev. B **53**, 11170-11175 (1996).

5. C.Y. Cha and J.H. Weaver, “Layer-by-layer Removal of GaAs(110) by Br,” J. Vac. Sci. Technol. B **14**, 3559-3562 (1996).

6. C.Y. Cha, J. Brake, B.Y. Han, D.W. Owens, and J.H. Weaver, “Surface Morphologies Associated with Thermal Desorption: Scanning Tunneling Microscopy Studies of Br-GaAs(110),” J. Vac. Sci. Technol. B **15**, 605-609 (1997).

7. J. Brake, C.Y. Cha, B.Y. Han, D.W. Owens, and J.H. Weaver, “Coverage-dependent Etching Pathways for Br-GaAs(110),” J. Vac. Sci. Technol. B **15**, 670-674 (1997).

8. B.Y. Han, C.Y. Cha, and J.H. Weaver, “Etch Pit Development and Growth on GaAs(110)” Phys. Rev. B **56**, 4966-4970 (1997).

9. C.Y. Cha, B.Y. Han, and J.H. Weaver, “Pulsed-laser-induced Etching of Br-GaAs(110),” Surf. Sci. Lett. **381**, L636-L643 (1997).

10. F.J. Williams, C.M. Aldao, Y. Gong, and J.H. Weaver, “Why Si(100) Steps are Rougher after Etching,” Phys. Rev. B **55**, 13829-13834 (1997).

11. Y. Gong, D.W. Owens, and J.H. Weaver, “Etching of Double-height-stepped Si(100)-2x1: A Study of Steps and Their Interactions,” Phys. Rev. B Rapid Commun. **53**, R16144-16147 (1996).

12. B.Y. Han, C.Y. Cha, and J.H. Weaver, “Layer-by-layer Etching of GaAs(110) with Halogenation and Pulsed-laser Irradiation,” J. Vac. Sci. Technol. A **16**, 490-493 (1998).

13. B.Y. Han and J.H. Weaver, "Spontaneous and Laser-enhanced Halogen Etching of GaAs," Special issue of Journal of Physics: Condensed Matter (in press).

14. S.J. Chey, Y. Gong, and J.H. Weaver, "Surface Morphologies of Br-etched Ge/Si(001)," Surf. Sci. (in press).

15. J.H. Weaver and C.M. Aldao, "Spontaneous Halogen Etching of Si," in *Morphological Organizations during Epitaxial Growth and Removal*, ed. Z.Y. Zhang and M.G. Lagally, World Scientific Series on Directions of Condensed Matter Physics (in press).

16. L. Huang, S.J. Chey, and J.H. Weaver, "Metastable Structures and Critical Thicknesses for Films Prepared at 50 K," Surf. Sci. Lett. (submitted).

17. K. Nakayama and J.H. Weaver, "Electron-stimulated Defect Creation on Si(100)-2x1," Science (submitted).

18. B.Y. Han and J.H. Weaver, "Laser Interaction with Br-GaAs(110): Etching and Atomic Desorption," Phys. Rev. B (in press).

19. J.J. Boland and J.H. Weaver, "A Surface Perspective of Etching," Physics Today **51**, xxx-xxx (1998 -- August issue).

Scientific personnel supported during this project:

1. X.-S. Wang, postdoc (now Hong Kong University of Science & Technology)
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9. D.W. Owens, graduate student (now heading start-up company)

OUTLINE OF RESEARCH FINDINGS

Statement of Problem Studied

This program emphasized physical and chemical etching of Si and GaAs and the growth of overlayers on these semiconductors. Scanning tunneling microscopy was used extensively to give atomic-level visualization that allowed us to develop an understanding of surface modification associated with material removal. Removal was accomplished by ion impact (physical sputtering) or the desorption of volatile species (thermally-activated etching). Studies of assisted etching dealt with mutual removal that was enhanced by laser irradiation.

Summary of Most Important Results

During Year I, we used energetic ions to modify surface morphologies for GaAs(110) and to establish a unique starting point for the subsequent growth of overlayers. Under the previous ARO program, we had shown that vacancies produced by low-energy ion beam sputtering at elevated temperature could diffuse to form single-layer vacancy islands. The possibility that ion sputtering could be used to modify the growth mode of Ge on GaAs(110) was then investigated by scanning tunneling microscopy. This was motivated by the fact that Ge/GaAs heterostructures have considerable potential for device applications but Ge nucleates as multilayer islands and nonuniform films. We reasoned that one way to enhance planarity would be to increase the density of nucleation sites, and we did this by bombarding with energetic ions at elevated temperature. Subsequently, we investigated Ge growth to determine the evolution of the overlayer. We found that Ge nucleates preferentially at steps associated with vacancy islands, significantly increasing the island density. This made it possible for the Ge film to cover the substrate at a smaller thickness than for an unsputtered substrate. Such growth can be understood in terms of a step energy model that takes into account the vacancy island size. Vacancy islands with lateral sizes less than 100 Å were most effective for such a growth modification because of their high curvature.

In Year I, studies were undertaken that examined surface roughness associated with material removal by physical sputtering of GaAs(110) at different temperatures. The effects of diffusion and kinetics on surface roughness were investigated by measuring the dependence of surface width and step density on the amount of material removed. Surface morphologies achieved after several monolayers of material were removed at 625 K were rougher on a small scale than those produced at 725 K but they were smoother on a large scale. The

increased large-scale roughness at high temperature was caused by increased diffusion on terraces and along step-edges but insufficient cross-step transport. The high step density created at low temperature enhanced cross-step transport. This mechanism, first proposed for the re-entrant layer-by-layer growth, was expected to cause the long-range roughness to increase with temperature for many solid surfaces after substantial sputtering or deposition for a certain range of temperature dictated by the details of diffusion and interlayer transport.

In many investigations in Years II (and III), we sought to define, understand, and control the relevant surface processes for Br-GaAs(110) etching. Etching reactions require the formation of volatile products derived in part from substrate atoms. Since formation and desorption processes have activation energies that depend on the particular surface site, we reasoned that the relative importance of the reaction pathways should vary with local morphology. In turn, the local morphology would change as material is removed. We then used STM to investigate Br-exposed GaAs(110) after heating to successively higher temperatures between 450 and 675 K. We found evidence for two distinct stages of surface modification. The first is associated with the creation of single-layer-deep etch pits on terraces. This sets in at about 500 K. The second stage, activated above 600 K, contributes to lateral enlargement of the etch pits. This stage can be related to etching via GaCl loss and desorption of As_2 (As_4). Etching in this expose-and-heat mode produces quite different surface morphologies than those reached with steady state etching because of the dependence of the reaction channels on surface-halogen concentration.

To quantify the coverage-dependent etching pathways, we analyzed STM images for surfaces heated to 700 K as a function of starting Br concentration. Areal analysis showed that the etch yield (number of substrate atoms removed per adsorbed Br atom) decreased as the initial coverage increased. This reflects competition between reaction channels involving GaBr and $GaBr_3$ evolution. We developed a kinetic model that demonstrated that the percentage removed by $GaBr_3$ increased with initial coverage but that most of the Ga atoms were removed as GaBr. Arsenic desorbs spontaneously at these temperatures.

Once the surface pathways were understood, we developed a protocol to achieve atomic layer-by-layer etching. We showed that such etching of GaAs(110) could be achieved by a two-step process. First, a Br-saturated surface was heated to develop an intermediate etched morphology with an irregular, partially removed top layer. Second, the surface was exposed to additional Br_2 at lower temperature to remove the residue of the top layer. Comparison of the morphology of this two-step process to that obtained after continuous thermal etching made it possible to discuss differences in the etching pathways related to the surface halogen concentration during thermal activation. The recipe that we developed should be applicable to atomic layer etching in many systems, and it reflects an application of basic science to a specific application.

Detailed studies of etch pit formation on GaAs(110) revealed that 80% of them that were 1-2 rows wide corresponded to pairwise removal of Ga and As from surface lattice sites. Once formed, these pits tend to grow along $[1\bar{1}0]$ and have ends that are equally likely to be bounded by either Ga or As atoms. Additional, etching occurs across adjacent rows. The resulting pits cross several zig-zag rows and have kinked $[1\bar{1}0]$ sides and irregular ends. When these pits grow larger, they exhibit kinked $\langle 1\bar{1}2 \rangle$ boundaries and hexagonal appearances. Rebonding of As atoms at pit boundaries to exposed second-layer As atoms was observed, and analysis of the pit boundaries indicates that there are equal numbers of As- and Ga-terminations. We suggested that etching along $[1\bar{1}0]$ involves removal of a Ga atom that was either a pit boundary atom or was next to a rebonded As boundary atom and that such processes are equally accessible. These were the first studies of the structure and growth of defects on terraces.

Building on these atomic-level insights, we undertook studies in year III of enhanced etching of GaAs(110) using Br in conjunction with laser irradiation. Several studies of laser-enhanced etching had shown the importance of electronic excitations of the reactant/surface ensemble, in which photocarriers participate directly in the reaction. In addition, relaxation and recombination of these photocarriers lead to a surface temperature rise and possibly thermally-activated etching. The relative importance of these two components, photocarrier-induced etching and laser heating, depends on the intensity and wavelength of the laser as well as the optoelectronic and thermal properties of the system under investigation. In the context of laser-solid interaction studies, several investigations had explored atomic desorption from defect sites on semiconductors surfaces during irradiation below the ablation threshold.

Our results showed that single layer etch pits were formed by irradiation of Br-covered GaAs(110) using 2.3 eV photons from a pulsed Nd-YAG laser. The pit morphologies produced in this way were very different from those obtained by spontaneous etching at elevated temperature or by thermal desorption of bromine-saturated surfaces. We explained this laser-induced etching by a combination of short-duration substrate heating and substrate-mediated charge transfer processes. Such etching occurs under conditions where surface diffusion of Br was minimal so that the pit profiles reflected the chemisorption structures. Continued laser irradiation caused Ga and As desorption from pit edges so that pits grew and thereby removed the remnant of the top GaAs layer. Hence, layer-by-layer etching of GaAs(110) was demonstrated through laser-induced etching and atomic desorption.

In order to investigate the interplay between photochemical and photothermal etching of Br-decorated GaAs(110), we undertook studies of surface morphological changes as a function of laser intensity, F, and substrate temperature. For clean surfaces, irradiation caused minimal changes. For surfaces decorated by islands of Br, however, irradiation created monolayer pits whose shapes reflected the chemisorption structures. The desorption yield followed a square law for low laser intensities ($F \leq 13.5$ mJ cm^{-2}) due to photochemical conversion of GaBr to volatile $GaBr_3$. 70-80% of the etch pits were composed of pair vacancies due to removal of gallium as $GaBr_3$ and arsenic as molecular As. These photochemical processes were enhanced by photothermal effects, even in the low intensity regime. Pit growth after Br depletion occurs via laser-induced desorption of Ga and As from pit edges. Growth along $[1\bar{1}0]$ was favored, reflecting the contrast in surface bonding strengths. Atomic desorption was initiated by electronic excitations, probably involving multiple electronic excitations. The yield varied as $F^{(3-3.5)}$. As with photoetching, it increased with base temperature. Both photoetching and laser-induced desorption resulted in stoichiometric removal, and the top layer could be removed by extended irradiation.

Finally, we started investigations of how electron irradiation would modify semiconductor surfaces and how these modifications would play a role in the larger arena of real world material removal. While electron beams have long been used to investigate the chemical and structural character of surfaces, knowledge about the atomic scale structural modifications that they produce is limited and largely circumstantial. Scanning tunneling microscopy offered an opportunity to explore these modifications, to relate them to the underlying physical phenomena, and to define new ways that they can be used.

We chose Si(100)-2x1 for our first studies of surface modifications with electrons because defect structures are relatively stable and because atoms ejected onto the terraces are kinetically captured at room temperature. Among the features stimulated by 2 keV electrons were single and extended dimer vacances, ad-dimers, and disordered structural moieties. Indeed, dimer vacancies develop on terraces and represent ~24% of the surface after exposure to only 2.3×10^{18} electrons cm^{-2}. Vacancy formation reflects hole localization associated with Auger decay and surface vibrational excitations. The dynamic behavior of these structures could be followed during controlled heating as isolated vacancies assembled into dimer vacancy lines and adatoms formed small epitaxial islands having c(4x4) symmetry. These modified surfaces will have higher reactivity to oxygen or etchants as processes enhanced by defects would be greatly accelerated. Analogous consequences of electron irradiation should be manifest for other materials, and their elucidation will define another way to achieve atomic scale engineering.

Several investigations dealt with etching of Si(100) surfaces on which Ge overlayers were grown. These showed similarities but also differences relative to Si(100). The most profound differences were related to the fact that dimer vacancy lines developed on Ge(100) because of the lattice mismatch of Si and Ge. For Ge overlayers on Si, these defects were the primary initiation points for reaction.

In Year III we wrote a major review article on Si etching, and we prepared a feature article on etching for Physics Today (August issue, 1998).